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## THE SHADDOCK, GRAPE FRUIT AND FORBIDDEN FRUIT.

BY CHAS. H. LAWALL.

Shaddock and Grape Fruit, *Citrus decumana*, Willd.; Forbidden Fruit, *Citrus Paradisi*, Macf.; natural order, Rutaceæ.

In October, 1895, the author of the following communication was requested by Prof. Trimble to take up the subject of the grape fruit or shaddock, and, after reviewing the literature, to write a paper considering the subject from its botanical, economical, pharmaceutical and chemical standpoints. Before submitting the results of his work, the author wishes to confess his inability to do justice to the subject, the magnitude of which was fully appreciated shortly after the work was commenced. It is hoped that this apology will atone for any incompleteness which may be evident to those who are thoroughly familiar with the subject.

In considering the flora of a given locality, the customary method of procedure is to arrange the plants in the following order: (1) Indigenous plants; (2) Plants which have become perfectly naturalized; (3) Plants under successful cultivation. According to this order of preference, the members of the *Citrus* genus would be of tertiary importance in most sub-tropical countries, which is clearly incorrect, as the commercial value of the fruits of this family entitles them, in many instances, to be considered as primary features in the flora of any locality.

Although the genus is of such a widespread character at the present time, it was originally indigenous to a small portion of Asia.

The introduction into most sub-tropical countries and the subsequent success which attended the cultivation of its members has given origin to numerous varieties, which renders the differentiation and systematic classification of varieties and species a task of great difficulty.

The generic name *Citrus* is mentioned by Wittstein as being of African origin. He also mentions several Greek forms of the word — *κίτρεα*, *κίτρη*, and *κίτρινον*.<sup>1</sup>

Many different opinions have been advanced concerning the exact locality of the origin of this important genus. Among the localities advocated by various authorities, may be mentioned India,<sup>2</sup> China,<sup>3</sup> Malay Islands,<sup>4</sup> Cochin China and Japan,<sup>5</sup> and tropical Asia.<sup>6</sup> The entire territory subject to dispute might easily be included in the term tropical Eastern Asia, which is specific enough for general use and has the advantage of being less open to criticism.

What is true of the genus in general is true of its members individually, consequently the origin of the shaddock is not definitely known. De Candolle<sup>7</sup> mentions that it does not occur wild in the Malay Archipelago, but that the number of varieties under cultivation would indicate an ancient origin. He also makes the statement (in opposition to Rumphius, who believed it to be a native of Southern China) that, while the species has a simple spoken name, *yu*, the written character appears to be too complicated for a truly indigenous plant. He mentions that indications of a wild existence are found in the islands east of the Malay Archipelago; that it is very common in the Friendly Isles and the Fiji Islands, where it covers the banks of the rivers, and concludes by saying that "it would be strange if a tree so much cultivated in Southern Asia should be naturalized to such a degree in certain islands of the Pacific, and scarcely be found elsewhere." In regard to India, it is stated<sup>8</sup> that there is no San-

<sup>1</sup> 1856, Wittstein, *Etymologisches Botanisches Handwörterbuch*.

<sup>2</sup> 1763, Linnæus, *Species Plantarum*; 1815, Pursh, *Hortus Catalogiensis*; 1862, Benthams and Hooker, *Genera Plantarum*.

<sup>3</sup> 1837, Jas. Macfayden, *Flora of Jamaica*; 1879, Chas. Pickering, *Chronological History of Plants*.

<sup>4</sup> 1875, J. D. Hooker, *Flora of British India*; 1888, *Encyclopedia Britannica*.

<sup>5</sup> 1828, Rees' *Encyclopedia*; 1866, Loudon's *Encyclopedia of Plants*.

<sup>6</sup> 1885, *Index Kewensis*, Vol. I.

<sup>7</sup> 1885, Alphonse de Candolle, *Origin of Cultivated Plants*.

<sup>8</sup> 1890, *Pharmacographia Indica*.

skrit name for the shaddock, which grows in abundance, and that in the vernacular it is *Batavi nebu*, owing to its having been introduced from Batavia. Pickering<sup>9</sup> thinks that the shaddock is the fruit referred to occasionally by authors of early times, "when lemons as large as watermelons" were seen by Abd-Allatif, and which was described by Ebn-Ayyas as "an orange of extraordinary bigness."

The name shaddock is derived from a sea captain of that name, who first carried the seeds to the West Indies, where it was soon under successful cultivation.<sup>10</sup>

The fruit of the members of this genus is a form of the berry, and is distinguished botanically by the term *hesperidium*; in this case the epicarp and mesocarp form a separable rind, and the endocarp sends prolongations inward, forming triangular divisions, to the inner angle of which the seeds are attached, pulpy cells being developed around them.

The terms grape fruit and shaddock are interchangeable as applied to the fruit in the markets of the cities of the northern United States, depending principally upon the size of the fruit, which, if large, is termed shaddock. In the West Indies the name grape fruit is also applied to a similar fruit of the genus, which will be described later. No reliance can be placed upon common names of plants or flowers, as it is well known that different sections of the same country have identical names for distinct species, and *vice versa*. The term shaddock is the only one employed by the greater number of writers who mention the fruit, the synonym grape fruit being seldom noticed even in dictionaries and works of reference. The Century Dictionary contains a curious contradiction in its definitions of the two terms: Under the word shaddock it states that "the shaddock proper is generally inferior to its smaller variety, the grape fruit, or pomelo, which is further distinguished by bearing its fruit in clusters." Under grape fruit it is stated that "it is a large variety of the shaddock, called grape fruit in the northern cities of the United States, presumably from its grape-like flavor." This valuable work of reference also gives the following additional list of names applied to the fruit in various localities: *Pumpelmoes, pampelmoose, pompel-*

<sup>9</sup> 1879, Chas. Pickering, *Chronological History of Plants*.

<sup>10</sup> 1828, Rees' *Encyclopedia*; 1837, Jas. Macfayden, *Flora of Jamaica*; 1866, London's *Encyclopedia of Plants*; 1879, Chas. Pickering, *Chronological History of Plants*.

*moes, pompoleon, pompelo, pomelo, pumelo and pummelo.* Many fruit dealers and importers of tropical fruit were interrogated regarding the matter; the majority of them stated that there was no difference between the grape fruit and shaddock excepting that of size.

There is a similar fruit which is claimed to be specifically different and which is frequently confused with the shaddock by botanical authorities. This is the Adam's apple, or forbidden fruit, known also by the names Paradise apple, pomo di Paradiso, pomo d'Adamo and Malum Assyriaca.<sup>11</sup>

This confusion was doubtless caused by Rumphius and Linnæus, who included it in their descriptions of the shaddock.<sup>12</sup> The most comprehensive study which was ever made and published regarding this subject was that of Jas. Macfayden,<sup>13</sup> who spent some years in the island of Jamaica, where the trees had been cultivated for a number of years previously. He differentiated the two species and applied the specific name *Paridisi* to the forbidden fruit. The following comparison of the characteristics of these two trees has been made, from his observations regarding them, in a manner which enables the reader to appreciate the differences at a glance :

## SHADDOCK.

*Citrus decumana.*

Tree 12 to 18 feet in height, with a flat crown and spreading branches, seldom spiny.

Leaves alternate, elliptic, rounded at both ends, sub-emarginate, crenulated, glabrous above, puberulous beneath, pellucid-punctate. Petioles winged, wings crenulated and minutely ciliate.

## FORBIDDEN FRUIT.

*Citrus Paradisi.*

Tree about 30 feet high; branches sub-erect, spiny; spines short axillary.

Leaves oval, rounded, crenulate, glabrous; petioles winged.

<sup>11</sup> 1591, D. Jacobi Theodor Tabernac, *Kreuterbuch*; 1597, Gerarde's *Herbal*; 1858, Robert Hogg, *The Vegetable Kingdom and Its Products*; 1885, Hehn and Stallybras, *The Wanderings of Plants and Animals*; 1823, Risso, *Essai sur l'histoire naturelle des Oranges, Bigaradiers*.

<sup>12</sup> 1763, Linnæus, *Species Plantarum*; 1824, De Candolle, *Prodromus Systematis Naturalis Regni Vegetabilis*, 1-539; 1858, Robert Hogg, *The Vegetable Kingdom and Its Products*; 1879, Chas. Pickering, *Chronological History of Plants*.

<sup>13</sup> 1837 Jas. Macfayden, *Flora of Jamaica*.



Flowers appear from February to May, and are dispersed in subterminal racemes, 3 to 9 flowered; the flowers are furnished with lanceolate bracts at point of insertion. Peduncles angular, pedicels pubescent.

Calyx irregularly 4-fid (rarely 5-fid).

Petals 4 (sometimes 5), oblong-obtuse, coriaceous, externally viridopunctate, furrowed longitudinally internally.

Stamens 30-35.

Ovary stipitate, globose, green and minutely pubescent.

Style terete and club-shaped.

Stigma subcapitate, turbinate.

Fruit very large with a thick rind.

Two varieties known.

Var. *a*. Maliformis. Fruit globose, pale pink pulp.

Var. *β*. Pyriformis. Fruit pear-shaped, pulp crimson.

The second variety is more esteemed, being sweet and juicy, and having only in a slight and palatable degree the acidity which abounds in the first.

Flowers peduncled, axillary, either solitary or in a raceme. From 2 to 6 bracts at the base of each pedicel. Peduncles glabrous,  $\frac{1}{2}$  inch long.

Calyx irregular, 5-fid, faintly ciliate.

Petals 4, linear-oblong, rounded.

Stamens 25.

Fruit sweetish, sub-acid.

Two varieties known.

Var. *a*. Maliformis, called forbidden fruit.

Var. *β*. Pyriformis, called Barbadoes grape fruit.

As is the case with the shaddock, the pear-shaped variety possesses most of the sweet principle, and is a preferable fruit.

That a difference does exist is evident from the above comparison. Mr. Macfayden applied the term grape fruit to the pear-shaped variety, and called the globose variety forbidden fruit. These terms may since have become interchanged, for the observations of a gentleman who spent some time in the West Indies show that at the present time the pear-shaped variety is called forbidden fruit, which was substantiated by several importers of tropical fruit, who also stated that the forbidden fruit is only in demand during the holidays, when it is used in fruit displays on account of its attractive appearance. Mr. Macfayden also observed that the trees in Jamaica are of an inferior character, from the fact of their having been raised from the seed, with no subsequent efforts to improve the quality by budding or grafting, a fact which had been mentioned some years previously by Thomas Martyn.<sup>14</sup>

The following descriptions of these fruits were furnished by a gentleman who had spent some time in the West Indies, and are

<sup>14</sup> 1797, Thomas Martyn, *The Gardener's and Botanist's Dictionary*.

interesting from the fact that they practically corroborate Mr. Macfayden's observations, made some fifty years before.

"Shaddock (*Citrus decumana*). This tree bears the largest fruit of the Citrus tribe. It grows to about the same height as the lemon or orange trees, with similar leaves, which are downy on the under surface. The flowers are larger than the orange blossoms, though similar. The fruit is of the shape of a huge orange, measuring 8 to 12 inches in diameter (large ones weigh from 7 to 8 pounds), and is covered with a pithy rind from  $\frac{3}{4}$  to 1 inch in thickness. The membrane that surrounds each 'fig' of the pulpy interior is very bitter, and is much thicker than is the case with the orange. It is customary to carefully avoid this when eating the fruit. As compared with the orange, the fruit is less juicy; a marked difference also exists in the flavor. Two varieties, having respectively red and white pulp, are known. There is little perceptible difference between them in flavor, the red is the sweeter, the white the more juicy of the two. The peel is candied and is in great demand among the inhabitants of the West Indies. This fruit should not be confounded with either the grape fruit or forbidden fruit."

"Grape fruit and forbidden fruit. These two trees of the Citrus family are so closely allied as not to be distinguishable in leaf or flower. The fruits are similar in the color of the pulp, which is pale yellowish. The grape fruit looks like a double-sized orange with a lemon-colored rind, while the forbidden fruit, of about the same size and color, is pointed at one end. The flavor of these two fruits is different from that of the orange, and, while they closely resemble each other, the forbidden fruit seems to have more of the shaddock flavor than the grape fruit, which is the more juicy. The rind of the grape fruit is thinner than that of the forbidden fruit, and, while hardly much thicker than the rind of an orange, it is tougher and stronger. These fruits are grown in the West Indies in much less quantity than oranges, but, while not sought after to any great extent for export, command a much larger price proportionately in the local markets. The skin surrounding the segments of the fruit is bitter, as in the case of the shaddock. While the shaddock, grape fruit and forbidden fruit are not equal to the Florida orange in richness of flavor, they are preferred to the West India orange, which is extremely acid."

The first mention of the shaddock is antedated many years by references to the forbidden fruit, which was fully described in many early works on plants, before the science of botany had evolved itself from the great mass of independent facts collected by early observers. Several very old references were found,<sup>15</sup> one of which is here quoted verbatim, with some correction of the antiquated spelling.

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<sup>15</sup> 1591, D. Jacobi Theodor Tabernac, *Kreuterbuch*; 1597, Gerarde's *Herbal*; 1640, John Parkinson, *The Theatre of Plants*, quoted above.

"Malum Assyria vel Pomo Adami. This tree groweth for the most part as great as the orange tree, yet sometimes it is no higher than the citron tree, and spreadeth fair great arms and branches, with few, and those short, thorns upon them. The leaves are fair and large, almost as great as those of the citron or lemon tree, pounced with holes in like manner. The flowers also are not much unlike, but the fruit that followeth is more like unto an orange, yet two or three times bigger, pale yellow rinded, thick, rugged and uneven, and with some rifts or chaps thereon, as if it had been bitten, from whence was obtruded that fond opinion unto the vulgar (for wise men would be ashamed of so ridiculous an opinion), that it was the fruit which Adam tasted in Paradise, and that, therefore, the marks should remain upon the whole kind forever after; thus have we three or four trees foisted into men's conceits by irreligious cozeners for Adam's apple. A spongy substance is next the skin of the fruit, which hath an acid sweet juice, yet not so pleasant as the others, and it hath round seeds among it like the citron."

The forbidden fruit is said to be used by the Jews of all countries at their feast of the tabernacles, and in many parts of Italy it was cultivated solely for that purpose.<sup>16</sup>

The shaddock undoubtedly has more decidedly specific characteristics than some others of the Citrus family,<sup>17</sup> some botanists even going so far as to declare that the only distinct species in the genus are the shaddock, on one hand, and all the other members on the other.<sup>18</sup> Few persons, however, would be willing to believe in the identity of the orange and lemon considered specifically. The fruit, as has been remarked before, is larger than any other fruit of the genus. It is described by some authors as sometimes exceeding 15 pounds in weight.<sup>19</sup> Linnæus<sup>20</sup> alludes to its large size in the following expressive manner: "*Malus aurantia fructu rotundo maximo pallescente caput humanum excedente.*"

At the present time, the shaddock is successfully cultivated in most sub-tropical countries; the demand for the fruit, while not large, is constant, and the tree is a very prolific bearer of fruit, so that it is a source of considerable profit to those persons who are directly interested in its cultivation. Two illustrations accompany this article, which are from photographs of fruit-bearing trees. The one of the entire tree shows the bearing-down of the branches

<sup>16</sup> 1885, Hehn and Stallybras, *The Wanderings of Plants and Animals*.

<sup>17</sup> 1880, Bentley and Trimen, *Medicinal Plants*.

<sup>18</sup> 1838, John Lindley, *Flora Medica*.

<sup>19</sup> 1891, Baron von Mueller, *Select Extra-Tropical Plants*.

<sup>20</sup> 1763, Linnæus, *Species Plantarum*.

on all sides from the heavy load of fruit. The illustration of the fruiting branch is a very good example of the manner in which the individual branches are sometimes crowded.

The liking for the fruit is an acquired one, in the majority of cases, as the impression usually formed, when the fruit is tasted for the first time, is that it resembles a poorly flavored orange more than anything else. Those persons who have cultivated a liking for it are, in most cases, enthusiastic in their praises of it, and the prophylactic and curative properties attributed to it by some of its devotees would cause it to rival the famous elixir vitæ in efficacy. It is supposed to be especially beneficial in dyspepsia and stomach troubles, and it is probably on this account that the demand for the fruit is constantly increasing. A recent newspaper article, in commenting upon the inferiority and scarcity of this year's supply, referred to the consumers of the fruit as "people who had formed the grape fruit habit," and that the matter is a serious one, from the fact that "it requires a certain amount of strength of mind to get accustomed to eating the fruit without sugar, and to learn to appreciate the bitter, aromatic, tantalizing flavor of the perfect fruit. That stage once reached, one is exposed to the temptation of casting away medicine bottles and devoting one's self to the fruit instead." The supplies in the markets of the northern United States are derived from the West Indies and Florida, the fruit from the latter source being preferred by those who are supposed to be able to judge correctly of its quality. The importations are small, compared with other fruits from the same ports, but are steadily increasing. The late frosts in the spring of 1895, which affected such a large area of the fruit-growing districts in the South, were especially destructive to the shaddock trees, so that the Florida crop was almost entirely destroyed, and the few that reached the Northern markets were inferior to those of former years, and commanded a much higher price. Some very good specimens were obtained after some difficulty, and were examined for percentage of glucose, citric acid, etc. While in search of samples of the fruit for examination, the author was fortunate in obtaining one of extraordinary size. It had been packed into a box of oranges for the purpose of occupying space, and was looked upon as an imposition by the receiver, who parted with it for a fraction of the sum it would have brought at retail. This specimen was globose, pale yellow in color, with a

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slightly roughened surface. The dimensions of the fruit are given below, as well as the results of the chemical examination:

Weight . . . . .	3,118 grammes (6 lbs. 14 oz.)	
Greatest circumference . . . . .	63 centimetres (24 $\frac{3}{4}$ in.)	
Greatest diameter . . . . .	22 centimetres (8 $\frac{1}{2}$ in.)	
Weight of peel . . . . .	907 grammes	} 29.08 per cent. 70.92 per cent.
Weight of pulpy interior . . . . .	2,211 grammes	
Juice . . . . .	1,200 cubic centimetres.	
Specific gravity of juice . . . . .	1.0319.	
Reducing sugar present . . . . .	2.00 per cent.	

100 cubic centimetres of juice required 11.25 cubic centimetres normal KOH for neutralization, using phenolphthalein as indicator, corresponding to 0.787 per cent. of citric acid.

Agitation with ether removed a crystalline principle from the juice. The quantity present was very small (0.0165 per cent.), but enough was obtained to take the melting point, which was 230° C. A similar principle was obtained in small quantities from the peel by extracting with cold water, and shaking out the aqueous extract with ether; this substance was of the same appearance, and had the same melting point.

Subsequent examination of specimens of smaller fruit gave slightly different results. Two examples will suffice to show the difference, which was not great, except in regard to the acidity:

NO. 1.

Specific gravity of juice . . . . .	1.0425
Reducing sugar present . . . . .	3.57 per cent.

100 cubic centimetres juice required 27.75 cubic centimetres normal KOH, phenolphthalein, corresponding to 1.94 per cent. citric acid.

NO. 2.

Specific gravity of juice . . . . .	1.040
Reducing sugar present . . . . .	3.84 per cent.

100 cubic centimetres juice required 18.91 cubic centimetres normal KOH, phenolphthalein, corresponding to 1.32 per cent. citric acid.

These analyses show that the differences in individual specimens of this fruit are no greater than in any other fruit which varies in quality of flavor and degree of acidity. The large specimen, which contained less sugar and acid, was a fruit of inferior flavor, which is not an uncommon occurrence in very large fruits of any species.

A syrup was made by using the juice and peel in the same manner as in the preparation of syrup of lemon. It was of an agreeable aromatic flavor, agreeably acid, with a not unpleasant bitter after-taste.

In summing up the various differences between these closely allied fruits, the author wishes to state the fact, mentioned previously, that common names are uncertain designations to go by. The literature herein submitted is contradictory in many respects. In the ancient descriptions of forbidden fruit no mention was found of a pear-shaped fruit, while that is a distinguishing character of that fruit as described at the present time. The term grape fruit was formerly used to denote a fruit of entirely different appearance, while now, it seems, from the testimony of persons whose observations were made on the spot, that it is a fruit closely resembling the shaddock in appearance, but still specifically different. The catalogues of several Southern nurserymen were consulted, with still more confusing effect. One described the grape fruit, or pomel, as *Citrus pomelano*, and offered two varieties. This same catalogue placed the forbidden fruit under the varieties of *Citrus decumana*, or shaddock. Another catalogue describes four or five varieties under the name *Citrus pomelana* (*decumana*). The extent to which hybridization is carried at the present time by fruit growers, who try to satisfy the popular craving for new varieties of old fruits (illustrated by the hundreds of varieties of apples now cultivated), makes gradations between species and varieties heretofore distinct, and renders classification almost impossible. The abundance of testimony is in favor of the grape fruit and shaddock being different varieties of the same species in the Northern markets; any difference which may exist is not noticed by the majority of persons who eat the fruit, and is apparently much slighter than is the case with the number of varieties of the orange with which we are familiar.

The author wishes to express his thanks to the following persons, who have been of service to him in his work upon this subject: Professor Trimble, for his many suggestions and valuable aid; Mr. Francis Lawton, of Jacksonville, Fla., for his descriptions of the fruit as known in the West Indies; and Miss Bertha L. De Graffe, for the photographs from which the illustrations accompanying the article were made.

## A SUBSTITUTION FOR RHUS TOXICODENDRON.

BY J. L. D. MORISON.

Contribution from the Botanical Laboratory of the Philadelphia College of Pharmacy.

The leaves of the common Virginia creeper, *Ampelopsis quinquefolia*, Mich., are sometimes substituted for those of the official *Rhus toxicodendron*.

This observation was recently confirmed in the examination of a quantity of the drug which was purchased from one of the most reliable wholesale houses; and this fact emphasizes the necessity of making a careful examination of all drugs of this class for the purpose of establishing their identity, judging of their quality, or detecting adulterations and substitutions.

A fraud of this nature may be easily detected by soaking up a sample of the leaves in water and carefully examining them. Those of the poison ivy are pinnately compound with three leaflets, while those of the Virginia creeper are palmately compound with five leaflets. The individual leaflets of the two plants differ also in form. The terminal leaflet of the poison ivy is long-petiolate, ovate or oval in general outline, with an acuminate apex, a somewhat wedge-shaped base, and a nearly entire margin; the lateral leaflets are nearly sessile, obliquely ovate, pointed, unequal at the base, with a variously notched or toothed margin, and have short petioles of nearly equal length.

When collecting this drug, the two plants may be easily distinguished. Both have the climbing habit, the poison ivy being provided with numerous adventitious roots that project from the sides of the stem, while the Virginia creeper produces disk-bearing tendrils opposite the leaves. The flowers of both plants are small and inconspicuous. Those of the poison ivy are yellowish-white, forming slender axillary panicles, while those of the Virginia creeper are greenish and occur in cymose clusters.

There is also a marked difference in the appearance of the fruits, those of the former being yellowish and drupaceous, and those of the latter small, purplish berries covered with a delicate bloom. The foliage of each is a bright crimson in the autumn, the leaves of the Virginia creeper, however, being browner and assuming a more vivid hue.

Finally, the poison ivy, as its name indicates, possesses an acrid juice that is intensely irritating to the skin and mucous membranes. On the other hand, the Virginia creeper is harmless, and may be handled with impunity.

The botanical characters of these two plants are thus seen to be markedly different, and but little difficulty is presented in distinguishing them.

### THE USE OF OXALIC ACID IN PRESERVING THE COLOR OF DRIED PLANTS.

BY J. HENRY SCHROEDER.

The importance of a well-selected herbarium is known to every botanist of the present day. It presents to him the most important specimens of the flora so far as known, and the better the specimens are preserved, the more valuable the collection. A very important, if not the most important, question is, how to preserve the natural color of the foliage, as well as the color of the petals.

No doubt, the rapidity with which the plant is dried greatly influences the preservation of the natural color; but in the course of time the great majority will fade, while others acquire different shades, some turn black, some brown and various other colors. This last change of color frequently takes place while the plant is being dried, and more rarely later on.

Not only the leaves, but the petals of most flowers change in the same way, thus lowering the value of the specimen to a considerable extent.

Nienhaus published in the *Schweizerische Wochenschrift für Chemie und Pharmacie*<sup>1</sup> his experience with oxalic acid as a preserving agent of the color of petals of dried plants. His theory was that ammonia in the air caused the fading of the color, and that it would be neutralized by this acid; therefore, he recommended that the plant be dried between filter-paper, which had previously been saturated in a 1 per cent. solution of the chemical, and then dried. Nienhaus experimented with the petals of *Papaver Rhæas*, and was very successful. According to some American writers, who have repeated his experiments, the results were entirely negative.<sup>2</sup>

<sup>1</sup> *Monatsblatt des deutschen Apotheker Vereins von New York*, March, 1895 (B. I, 11).

<sup>2</sup> *Bulletin of Pharmacy*, June 1895, p. 269.



Since then I have had occasion to study the value of Nienhaus' process, and have found that not only the petals are well preserved, but that a 3 per cent. solution will also preserve the color of the leaves. In the hope that the results may be of interest to collectors of plants, I think it proper to bring it to their notice.

Several specimens, which had been dried by the aid of 1 per cent. oxalic acid, did not give me as good results as I had hoped to obtain, and I then determined to study the value of different strengths of the solution, and find out which would be most suitable to be employed in average cases.

For this purpose I saturated some gray felt paper with solution of oxalic acid, varying in strengths from 1 to 5 per cent., and dried.

Leaves of different texture were selected, dried between the thus prepared paper at ordinary temperature, changing paper once in twenty-four hours.

Leaves of a *thin* texture were well preserved with a 2 per cent. solution; not so well with that of 1 per cent. Those dried between 3 to 5 per cent. paper did not differ materially in appearance from those dried with that of 2 per cent. strength.

Leaves of a *thick* texture were best preserved with 3 per cent. of the acid, although the 4 and 5 per cent. solutions showed no disadvantage.

The leaves of aquatic plants were best preserved with 2 or 3 per cent. of acid; the 1 per cent. specimens turned dark, and with 4 or 5 per cent. they were almost black in one case, while in other aquatics I could observe no difference between any of the specimens; they all had kept well.

These results suggested to me that paper saturated with a 3 per cent. solution of oxalic acid might be used with more advantage for the majority of plants than a 1 per cent. solution, as recommended by Nienhaus. It is not unlikely that the kind of drying-paper used influences the results to some extent.

Nienhaus recommended filter-paper to be employed; in fact, the heavy felt paper mostly employed in this country is not often used in Germany for drying purposes; the botanists there prefer a very much thinner gray paper.

In almost all cases where a 3 per cent. solution of oxalic acid was employed, I have obtained satisfactory and encouraging results,

except with some members of the Umbelliferæ, which turned dark when thus treated.

I had not the opportunity of making further experiments with them, and do not know their behavior when dried in paper without the aid of oxalic acid.

The leaves of *Phytolacca decandra*, under ordinary circumstances, turned to a very dark color; when dried by the aid of a 3 per cent. solution of oxalic acid they remain green.

The leaves of *Geranium maculatum* commonly turn reddish-brown; when preserved with 3 per cent. of the acid they remain green.

The leaves and petals of *Baptisia tinctoria* almost invariably turn black when dried in the ordinary way; when preserved with 3 per cent. oxalic acid, the change is much less pronounced and the petals remain yellow.

In all specimens the color of the petals was unchanged.

The results which I have obtained by this process lead me to the conclusion that it may be employed with decided advantage in almost all cases, and I will briefly state the method I have employed: Heavy gray felt paper was thoroughly saturated with a 3 per cent. solution of oxalic acid, and dried. This, when done at ordinary summer temperature, required about twelve hours. Directly between the thus prepared paper I placed the plant; in case the petals were very delicate, they were protected by a very thin piece of paper to prevent imprints from the rough felt paper. The latter was changed once in twenty-four or thirty-six hours, until the plant was thoroughly dried, and it was then mounted in the ordinary way. If possible, the plants should be placed in the press at the time of collection, or carried in an air-tight box and moistened before pressing.

Up to the present date I have not had the opportunity of studying by experiments to what extent plant colors are really injured by ammonia, but I hope to be able to report upon this question at a subsequent date.

PHILADELPHIA, February, 1896.

# BITTERLESS CASCARA SAGRADA.

BY HENRY B. GILPIN.

The extended use of *Rhamnus Purshiana*, or *Cascara Sagrada*, as it is more usually termed, has led to frequent attempts to improve the various pharmaceutical preparations of this valuable drug. The researches of various investigators have proved that the laxative properties of the bark are undoubtedly due to principles similar in their medical properties, and, to a considerable extent, in their chemical composition, to those contained in rhubarb and frangula. *Cascara Sagrada* differs materially, however, from rhubarb on account of the presence of a bitter, crystalline principle. Meier and Webber assert that the drug also contains a ferment, to which is attributed the griping effects of the fresh bark, and there is little doubt that our Pharmacopœia should insert in its definition a requirement that the bark should be kept at least one year after its collection before being used, as is the case with the definition of frangula bark. The bitter principle has been regarded by many as objectionable, and as interfering with the continued use of the drug as a laxative. The resinous constituents are, without doubt, the cause of the purgative action. The pharmaceutical problem which is presented, then, is to provide a preparation which will contain all the resinous constituents, but free from bitterness; and with this object in view, a process has been devised for making a powder which may be used for the liquid preparations, such as fluid extract, tincture, syrup, etc.

## BITTERLESS POWDERED CASCARA SAGRADA.

	Grammes.
Take of powdered <i>Cascara Sagrada</i> . . . . .	500
“ licorice root . . . . .	110
Magnesia (calcined) . . . . .	10
Powdered cloves . . . . .	5

The powders are thoroughly mixed, transferred to a “power kneader,” and then moistened with sufficient water; after being thoroughly kneaded, the mass is transferred to a closed drying chamber, and subjected to a uniform temperature of 180° F. for forty-eight hours. The moisture is then permitted to escape from the chamber, and the powder thoroughly dried, after which it is repowdered and sifted.

It will be observed that aromatics are added with a view to improving the taste, and the preparations made from the powder are free from bitterness, whilst the laxative properties are unimpaired.

BALTIMORE, February 12, 1896.

A CONTRIBUTION TO THE KNOWLEDGE OF SOME  
NORTH AMERICAN CONIFERÆ.

BY EDSON S. BASTIN AND HENRY TRIMBLE.

(Continued from page 79.)

## PINUS PALUSTRIS.

## CHEMICAL COMPOSITION.

For the purpose of investigating the constituents, other than the oleoresin, of *Pinus palustris*, two specimens were obtained; one, consisting of young shoots, was procured in Philadelphia, just before the holiday season, when considerable quantities of the tops of young long-leaved pines are brought from North Carolina and sold in Northern cities. The present sample was probably collected in December, as it was quite "green" when received. The bark and leaves of this specimen were investigated. The other sample was obtained from Dr. Charles Mohr, of Mobile, Ala., and was also collected in December. It was taken from trees of medium size and age, and consisted largely of cork. The following are the percentage results for moisture, ash and tannin:

	Moisture.	Ash in Absolutely Dry Material.	Tannin in Air-Dry Material.	Tannin in Absolutely Dry Material.
Leaves of young tree . . .	4.92	1.91	7.54	7.93
Stem bark of young tree . .	7.46	1.34	17.49	18.89
Trunk bark of old tree . . .	10.62	0.80	5.04	5.64

The tannin in all cases gave a green color and precipitate with ferric chloride, a yellow precipitate with bromine water and a purplish precipitate with lime water, thus indicating its similarity to those already studied in this natural order.

The leaves readily yielded their green coloring matter to absolute alcohol, to which solvent they also imparted an acid reaction similar to that obtained from the leaves of the other species examined.

Mucilage was present in both leaves and bark, but in relatively small proportion.

The ash, in all cases, was composed chiefly of calcium phosphate with some sulphate and carbonate.

The oleoresin is by far the most important constituent of the long-leaf pine. According to H. Mayr<sup>1</sup>, the sap wood yielded 2.65, and the heart wood 11.09 per cent. of resin, and he ventured the

<sup>1</sup>*Das Harz der Nadelhölzer*, Berlin, 1854.

statement that no German, and, apparently, no other American pine, contained as much resin.

No attempt has been made in the present case to investigate the chemistry of this oleoresin, although such a work is sadly needed. Some progress on this subject was recorded by R. G. Dunwody<sup>2</sup>, who also described the turpentine industry. J. H. Long<sup>3</sup> has added considerable to our knowledge of the physical constants of turpentine oil. He has pointed out the fact that no attempt is made by turpentine producers to keep the products from different species of pine separate, which, no doubt, accounts for the variable results obtained by different investigators in pine oils. This, Professor Long<sup>4</sup> has more recently (1894) kept in mind in a further contribution, in which the oil was distilled from the products of single trees. The results are more uniform and satisfactory. Research is still needed on all the products from the *Pinus palustris*, since it furnishes the largest proportion of the world's supply of resin and its products.

The subject of resinous products and the turpentine industry will be considered later, after the other pines which furnish the balance of the supply, have been considered.

It may be appropriate to consider at this point

#### THE PHYSIOLOGY OF THE RESINS,

since these compounds are most abundant in the long-leaf pine. As long ago as 1867, Hlasiwetz<sup>5</sup> pointed out the relation between the decomposition products of the resins and the tannins.

It is pertinent to note in this connection that all the facts observed regarding the oleoresins of the pines show that they are very closely associated with the tannins. While this, of itself, does not prove that the former are derived from the latter, the nature of the association is such as to strongly suggest such a conclusion. For example, a secretion reservoir begins in a cluster of a few thin-walled cells, rich in granular protoplasm, which early shows an abundance of tannin. Later on, oleoresinous matters appear, and, as these increase in quantity, the tannin and the protoplasm dimin-

<sup>2</sup>AM. JOUR. PHAR., 1890 p. 284.

<sup>3</sup>*Journal of Analytical and Applied Chemistry*, 6, 1 and 7, 99.

<sup>4</sup>*Journal of the American Chemical Society*, 16, 844.

<sup>5</sup>Ueber die Beziehung der Gerbsäuren, Glucoside, Phlobaphene und Harze, *Sitzb. d. mathem.-naturw. Cl.*, 55, (II) 575, *Annalen*, 143, 290.

ish, and finally the walls break down, leaving a cavity or intercellular space containing the oleoresin. In the meantime, cells immediately bounding this space are gradually undergoing similar changes, and so on, as long as the secretion reservoir continues to grow. So, if any well-developed secretion reservoir, with the surrounding cells, be examined, there will be found: (1) a central space filled with oleoresin; (2) an area of cells immediately surrounding this, which contain much oleoresin, and little tannin and protoplasm; and (3) still farther exterior, a layer of very granular cells, rich in protoplasm and tannin, but containing very little volatile oil or resin. In *Pinus palustris*, a species especially rich in oleoresin, it is also clearly seen that the older medullary ray cells of the wood are filled with oleoresin, but contain but little tannin, while the reverse is the case with the younger medullary ray cells. There is no denying the fact that, as the resin increases, the tannin diminishes, whatever the conclusion we may draw from the circumstance.

The view that tannic matters are derived from starch apparently obtains no support from these observations on the pines. A very little fine-grained starch was found in the stems of the pines investigated; it was never abundant, while in the roots it was usually present in considerable quantity. On the other hand, as respects the tannin of the different species, very little difference was observed between the roots and stems, either as to the quantity or as to the distribution of the tannin. No indication whatever was found that as starch decreases tannin increases, or of any quantitative relation between the two substances. The facts do, however, show an intimate relation between the tannin and the protoplasm. It is abundant in all parts of the protoplasm, even in the nucleus, though it does not appear to exist, normally at least, except in very minute quantity, in the cell wall. After the death of the tissues, however, it rapidly diffuses into the cell walls. Tannin was found even in the protoplasm of meristem cells, though apparently in less abundance than in many of the more mature cells. In the living cell it seems to be most abundant in the ectoplasm. While this does not positively disprove that tannin is derived from a carbohydrate, the probability is at least suggested that it is derived from the breaking down of the proteids during the processes of cell growth. The process is probably complex, but no guess is ventured as to what the various chemical stages of the process are.



The investigation has thus far thrown little or no light on the question of the functions of tannin, whether it is physiologically useful or whether it is to be regarded as wholly a waste product of tissue metamorphosis.

As respects the origin of resin from volatile oil, the microscopic study of the pines, especially of *P. palustris*, seems to afford pretty clear evidence.

Old secretion reservoirs were observed to contain irregular solid or semi-solid masses of oleoresin, in which apparently the resin is the predominating element, while young reservoirs contain a more fluid oleoresin in the form of globules. Moreover, in the secretion cells immediately surrounding the reservoirs the oleoresin is in globules and evidently very fluid. In fact, in passing from the younger to the older portions of the secretion tissue there appears to be every gradation between a very liquid volatile oil and a semi-solid oleoresin.

There appears to be no question that the oleoresin is to be regarded as wholly a waste product. It clearly can play no part in the process of nutrition. Its only use is that of protection against the destructive forms of animal life and against vegetable parasites.

It is highly antiseptic, it protects mechanically against injurious insects, and its taste and effects are disagreeable to most of the higher animals.

#### PINUS LONGIFOLIA, ROXB.

##### EMODI PINE, CHEER PINE.

Through the courtesy of Mr. A. E. Wild, conservator of forests, Bengal, India, we have been able to examine the tannin percentage and its character in a number of coniferous barks from that section. This one is introduced here on account of its close relation to our own *P. palustris*.

For the history, description, etc., of *P. longifolia*, we are indebted to the Pharmacographia Indica, Part VI, and to the ninth edition of Mueller's Select Extra-Tropical Plants, just received.

The Cheer or Chir pine is a tall, handsome tree, with a straight, branchless trunk for 50 feet, the whole tree attaining a maximum height of 100 feet, with a stem girth of 12 feet. It is indigenous to Afghanistan and the Northwest Himalayas. The turpentine yielded by this tree is much prized by the natives. Incisions are made in the sap wood, and from 10 to 20 pounds of a good quality of turpentine are obtained the first year; about one-third that amount is collected the second year, after which the tree either dies or is blown down.

As with our native long-leaf pine, the resin is the most important con-

stituent; 56 pounds of the crude material, when distilled with water, yield 8 pounds of a colorless limpid oil. This oil, according to Lyon, has a specific gravity of 0.875 at 28° C., boils at 155° C., and is dextrorotary.

The sample of bark obtained by us yielded the following results for tannin and ash :

	Per Cent.
Moisture . . . . .	11.75
Ash in absolutely dry bark . . . . .	2.33
Tannin in absolutely dry bark . . . . .	14.62

This tannin gave all the qualitative reactions indicating its identity with that from oak bark, and on combustion it yielded the following percentages :

	Per Cent.
Carbon . . . . .	62.50
Hydrogen . . . . .	5.28

These figures are a little higher than those yielded by oak bark tannin, but the small amount of material at our disposal prevented our purifying it to quite the extent we desired.

The bark of this tree is used by the natives for tanning, the branches are used for torches, and the resinous wood, besides yielding turpentine, is valuable for building purposes.

(*To be continued.*)

## ARISTOLOCHIA ARGENTINA.<sup>1</sup>

BY DR. O. HESSE.

The principles isolated from different species of *Aristolochia* have received various names by investigators, although, no doubt, identical in some instances. Walz<sup>2</sup> gave to the resinous products from *Aristolochia clematis* the names aristolochic acid ( $C_{11}H_{16}O_3$ ) and clematitin ( $C_9H_{10}O_6$ ). The latter is thought to be identical with serpentarin or aristolochin, the poisonous principle obtained by Chevalier<sup>3</sup> from the root of *aristolochia serpentaria*. Frickinger<sup>4</sup> obtained from the young underground shoots of *Aristolochia clematis* a crystalline substance which he named aristolochia yellow, but its individuality was not established. Not long ago, Dymock and Warden<sup>5</sup> obtained from *Aristolochia indica* a resin of a basic nature. Later, Hesse published his, then, incomplete investigation of *Aristolochia argentina*<sup>6</sup> showing the presence of an ester, probably palmityl phytostearin, an alkaloid—aristolochine—and a yellow crystalline body

<sup>1</sup> Abstracted from translation in *Pharmaceutical Journal*, January, 1896.

<sup>2</sup> *Jahrb. f. prakt. Pharm.*, xxiv, 65; xxvi, 65.

<sup>3</sup> *Journ. Pharm.*, 2, v, 565.

<sup>4</sup> *Repert. für Pharm.*, 3, 7, 1.

<sup>5</sup> *Pharm. Journ.*, 3, xxii, 245.

<sup>6</sup> *Ibid.*, 3, xxii, 551.

—aristin. Previously, however, Pohl had investigated various species of *Aristolochia*, and described a finely crystalline yellow substance under the name of aristolochine. But as this substance is of an acid nature, it is thought better to call it aristolochic acid, so as not to confuse it with the alkaloid.

Hesse has since continued his investigations, and thereby made clearer the chemistry of these substances.

*Aristolochine*.—This principle is obtained by treating the roots with soda and afterward extracting with alcohol. The residue left after distilling off the alcohol is treated with sodium carbonate and ether, and, on shaking the ethereal solution with dilute tartaric acid and decolorizing with charcoal, the base is precipitated on the addition of ammonia and separated with ether. It is a colorless, distinctly crystalline substance. In alcoholic solution it turns litmus paper blue and completely neutralizes acids, but the salts are amorphous.

*Indifferent Substance*.—When atmospheric air containing ammonia is passed through an ether extract of the crushed roots, the liquid deposits red crystals. Afterwards the ether is shaken with acid, and, on distillation, a residue remains which yields crystals of palmityl phytostearin,  $C_{42}H_{74}O_2$ , melting at  $82^{\circ} C.$ , and a minute quantity of aristolin,  $C_{15}H_{28}O_3$ .

*Aristinic Acid* ( $C_{18}H_{13}NO_7$ ).—The red deposit from the ammoniacal extract consists principally of the ammonia salt of this acid. It forms greenish-yellow laminæ and needles, melting at  $275^{\circ} C.$ , with decomposition.

*Aristidinic Acid* ( $C_{18}H_{13}NO_7$ ).—This acid remains in the acetic acid solution from which aristinic acid has been separated. It is soluble in ether and crystallizes in small needles.

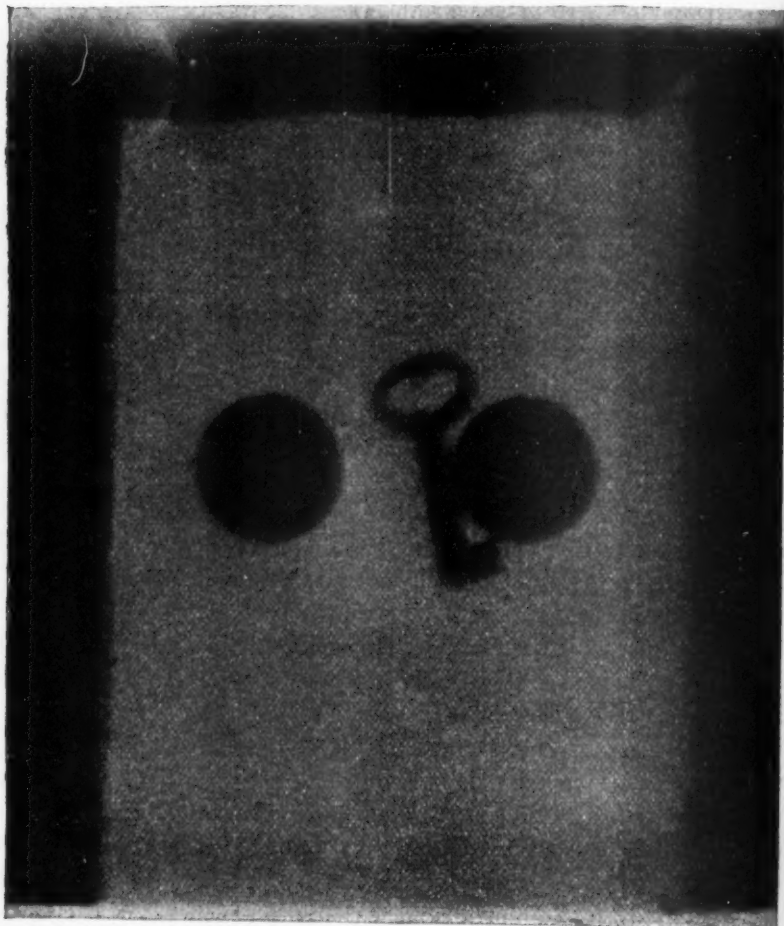
*Aristolic Acid* ( $C_{15}H_{13}NO_7$  or  $C_{15}H_{11}NO_7$ ).—On treating the alkaline solution from which the acids previously mentioned have been separated with hydrochloric acid, and afterward shaking with ether, an orange-yellow crystalline residue is obtained on evaporating the solvent. The crystals melt between  $260^{\circ}$  and  $270^{\circ} C.$  This acid dissolves in strong sulphuric acid with dark green color, this character indicating relation to the other acids and also to the aristolochine of Pohl.

These substances probably exist in other varieties of the genus *Aristolochia*, but an examination of the roots of *Aristolochia longa* has yielded only negative results.

## ARE THEY ROENTGEN RAYS?

BY EDSON S. BASTIN.

Years ago, when the writer dabbled somewhat in amateur photography, he observed that, when his plate-holders containing dry plates were exposed to direct sunlight, fogging was the result. It



Photograph by direct sunlight through Opaque Slide of Plate-Holder.

was then supposed that the plate-holders must have been defective; but since the discovery of the new rays by Roentgen, it occurred to the writer that the effects observed may have been due to these rays in the sunlight; so it was determined to subject the matter to

the test of experiment. Accordingly, the plate-holder of a Corona camera, whose slides are of hard rubber, and another holder having a pasteboard slide, were taken for experiments. In one experiment, two copper pennies and a small brass key were fastened to the surface of one of the slides, beneath which was placed an ordinary dry plate, one of Seeds'. The margin of the plate-holder was covered with black paper, to guard against possible fogging by leakage of light, and the holder was exposed for two hours to direct sunlight. On development, there was a very distinct shadow picture of the pennies and key.

Further experiments showed that similar shadow pictures could be taken through two thicknesses of ordinary pasteboard, and through sheets of vulcanized rubber, 1 millimetre in thickness, but opaque to the eye. This was accomplished by means of gas and kerosene light, as well as by sunlight, though, of course, in these cases longer exposure was required than when direct sunlight was employed. Various experiments, however, showed that the rays did not agree in their properties with the X-rays of Roentgen. They can be reflected and refracted, and they penetrate only with the greatest difficulty a sheet of black paper. They are probably only the ordinary actinic rays, which have a power, heretofore unsuspected, of penetrating certain substances opaque to the visual rays. The facts, however, are of great practical importance to manufacturers and dealers in dry plates and to those engaged in the photographic art generally.

PHILADELPHIA, February 22, 1896.

## THE GLACIAL ACETIC ACID TEST FOR GURJUN BALSAM IN BALSAM COPAIBA.

BY LYMAN F. KEBLER.

In the August number of this<sup>1</sup> JOURNAL, I reported on the efficacy of the above test. The test, as outlined there, is a modification of the original one. In the original<sup>2</sup> test, the balsam copaiba is dissolved in the glacial acetic acid and the nitric acid then added to the mixture, while, in the modification, the nitric acid is mixed with the glacial acetic acid, and the balsam carefully added to this mix-

<sup>1</sup>1895, AM. JOUR. PHARM., 67, 394.

<sup>2</sup>1895, *Am. Druggist*, 27, 5.

ture. I also take note of the zone of contact; this renders the modification test more delicate than the original. This note is presented here because it is maintained that the test as modified is too delicate. Thus far I have failed to secure a genuine sample of balsam copaiba that responded affirmatively with this test. I requested the party who informed me concerning the shortcoming of the modified test to forward me a sample of the genuine balsam copaiba with which this test indicated gurjun balsam. Thus far I have not received it, and probably never will. Any reader meeting with such a sample of balsam copaiba will do me a great favor by sending a portion to me.

305 CHERRY STREET, PHILADELPHIA.

## THE MANUFACTURE OF ACETONE AND OF ACETONE-CHLOROFORM FROM ACETIC ACID.

BY EDWARD R. SQUIBB, M.D.,<sup>1</sup> of Brooklyn, N. Y.

Just one year ago, January 11, 1895, the writer read a paper before this Society, upon "Improvement in the Manufacture of Acetone," and this paper was published in the *Journal* for March, 1895, at page 187.<sup>2</sup> The improvement claimed consisted in the use of acetic acid instead of acetates, and in the use of a rotary still for the decomposition. The results given were obtained from a model apparatus on a table.

During the year that has elapsed since that paper was read, a large rotary still, 12 feet in length by 2 feet in diameter, has been set up, and this has decomposed, in 126 hours, about 1,700 pounds of absolute acetic acid, giving about 90 per cent. of the theoretical yield of acetone, against about 80 per cent. in the small apparatus.

But the patentees of the processes for making acetone from acetates object to the use of this process and apparatus as being in conflict with their patents.

The acetone produced was converted into chloroform by the Watts (Siemerling) proportions of material, in an apparatus described by the writer in 1857 (*Ephemeris*, Vol. IV, No. 1, p. 71), and used

<sup>1</sup> Read before the N. Y. Section of The American Chemical Society, January 10, 1896. From Squibb's *Ephemeris*, Vol. IV, p. 1743.

<sup>2</sup> AM. JOUR. PHARM., 67, 144.



for many years in making chloroform from alcohol, and this is also objected to.

Under these circumstances, it seems necessary to find out what has been done in the past upon this important subject, and what may be the relations of past work to the present conditions, and in this it is hoped the Society may be interested.

#### ACETONE.

It is impossible to determine when or where acetone was first made and used.<sup>3</sup> According to the authority last given, after the time of Boerhaave, in 1732, "the body was but little investigated until 1805, when Trommsdorff stated that, on distilling acetate of potash or soda, a liquid was obtained which stands between alcohol and ether." In 1807 the Brothers Derosne, in Paris,<sup>4</sup> studied its properties; and, in 1809, Chenevix<sup>5</sup> demonstrated that this substance was obtained by the dry distillation of any one of the acetates.

The correct composition of acetone was first given by Liebig<sup>6</sup> and Dumas.<sup>7</sup>

Further investigations by Kane, 1838, and by Chancel, Williamson, Chiozza, Freund, Wanklyn, and others, still more definitely established the sources, character and properties of acetone, and gave it a definite chemical and economic position, so that its production or manufacture by the dry distillation of acetates was as well known as the production of alcohol by distillation from fermented sugars, as early as 1848, when Böttger refers to it as a market article in common use. Wackenroder,<sup>8</sup> in 1848, states that since acetone is quoted on the price lists at 10 sgr. (Silbergroschen) per ounce, the preparation of chloroform from it is well worth recommending.

In "Handwörterbuch der reinen und angewandten Chemie herausgegeben von Dr. J. Liebig, Dr. J. C. Poggendorff und Dr. Fr.

<sup>3</sup> See Wurtz' Dictionnaire de Chimie, 1873, tome I, p. 31. Gmelin, Handbook of Chemistry, 1855, Vol. IX, p. 1. Roscoe and Schorlemmer, A Treatise on Chemistry, 1882, Vol. III, Part I, p. 568.

<sup>4</sup> Ann. de Chimie, t. LXIII, p. 267.

<sup>5</sup> Ann. der Physik, Vol. XXXII, p. 191.

<sup>6</sup> Ann. Pharm., Vol. I, p. 223.

<sup>7</sup> Ann. de Chim. et de Phys., t. XLIX, p. 208.

<sup>8</sup> Archiv. der Pharmacie, Vol. LIII, p. 273.

Wöhler—Redigirt von Dr. Hermann Kolbe, Braunschweig," 1842, Vol. II, p. 1018, is the following (translated) statement:

According to Justus Liebig and Pelouze, the best thing to use for the preparation of acetone is concentrated acetic acid, which in the state of vapor is conducted through a heated tube of glass, porcelain or iron, which, for the sake of increasing surface, is filled with pieces of charcoal, and the products of decomposition are condensed in the usual way. The tube should be heated only to incipient redness; at a higher temperature, only empyreumatic oils, combustible gases and charcoal are obtained as the products of the decomposition.

Besides the citations given, the literature on the preparation, properties and reactions of acetone is very copious and definite up to about 1853. After this date the papers published are comparatively few, leading to the inference that the substance had reached a definite position and gone into general use.

In a paper by Prof. Samuel P. Sadtler, Ph.D., "On Recent Improvements in the Methods for the Manufacture of Chloroform," published in *THE AMERICAN JOURNAL OF PHARMACY* for July, 1889, p. 321, the following statements are made:

"The old process of manufacture by the action of bleaching powder upon alcohol has given way to what is now termed the 'acetone' process. This is not, however, a new discovery. Liebig, in 1832, in following up his first account of the properties of the newly discovered 'chloride of carbon' (chloroform) mentions that it can be gotten in very large quantities by the action of bleaching powder upon 'pyroacetic spirit' (acetone) as well as from alcohol. That alcohol has, all this time, been preferred to acetone as a material from which to prepare chloroform is due mainly to the fact that only in recent years has acetone been prepared pure in quantity, but also to the erroneous statement of Siemerling, quoted in the works of reference, like Watts' Dictionary of Chemistry, that only 33 per cent. of chloroform could be gotten from acetone by the action of bleaching powder." . . . "The manufacture of a purer grade of acetone than that then in use for solvent purposes having been begun in Germany in 1881, on the part of the 'Verein für Chemische Industrie,' Liebig's old suggestion for the manufacture of chloroform from acetone was taken up by the 'Verein Chemischer Fabriken,' Mannheim, Germany, in the beginning of 1882, and a

year later by the first-mentioned company, which made the acetone for both."

From these references it will be seen that the reactions involved in the production of acetone, and the constitution, character, properties and reactions of acetone, had been long and well known prior to 1848, and that it had been made and utilized on a large scale prior to 1882; and further, that it had been produced both by the dry distillation of acetates and by the wet distillation of acetic acid, as a matter of open knowledge and practice.

This condition of the scientific knowledge of an important chemical substance throughout France and Germany—and throughout the scientific world—makes it very certain that the chemical industries, which depend upon such knowledge for their origin and progress in general, but do not publish their processes—availed themselves of this knowledge and of this chemical agent.

In June, of 1886, application was filed in the U. S. Patent Office, and two years later, in July, 1888, Letters-Patent, No. 385,777, were issued to Gustav Rumpf, for the invention of "a new and useful Improvement in the Manufacture of Acetone," and from the specifications and claims of this patent the following extracts are made:

"In making acetone by dry distillation of acetates—as acetate of lime—it has, before my invention, been thought possible to obtain only less than half the acetone.

"Dr. Hermann Hager, in his *Handbuch der Pharmaceutischen Praxis*, published in Berlin in 1882, states, under the head of 'Acetone,' 'that it is possible to obtain an average yield from chemically pure acetate of lime, only 15 per cent. of acetone, while the theoretical yield from chemically pure acetate of lime is 34 per cent.

"I have discovered that if the acetates are subjected for distillation to a low heat and approximately uniform temperature, and the process extended over several hours, the yield of acetone will be greatly increased, and will approach very nearly the theoretical yield of any particular acetate, which, in the case of good gray or commercial acetate of lime, is about 27 per cent. I have also discovered that in the process of subjecting acetates in a closed vessel to heat applied externally to the vessel for distilling acetone from the acetates, the desired slowness of distillation and uniformity of temperature may be secured by stirring the acetates so that all por-

tions of the mass will be subjected to the heat resulting from direct contact with the bottom of the vessel, and by admitting free steam from time to time into direct contact with the acetates in case of any undesirable rise in temperature within the vessel.

"My invention consists in an improvement in the method of obtaining acetone from acetates by destructive distillation, consisting in subjecting the acetates in a closed vessel to slow destructive distillation at a low and approximately uniform temperature, and it is also well to stir the acetates during such distillation."

The claims are to—

"The improvement in the method of obtaining acetone from an acetate, consisting in subjecting the acetate in a closed vessel to slow destructive distillation at a low and approximately uniform temperature."

This first broad claim is based, not upon the chemical reaction, which was well known, nor upon the destructive distillation by heat, which was a well-known process, but upon an improvement in the apparatus and management, by which the yield of acetone was alleged to have been increased. But the evidence upon which the increase is claimed is an erroneous statement quoted from Hager—erroneous because it is hardly practicable, through any ordinary degree of want of knowledge and skill, to obtain so little as 15 per cent. of acetone from acetate of lime.

The second claim is to a stirrer in its effects on the process. But a stirrer is a device so common in chemical processes that no such application of it can be considered original or new.

The third claim to the effect of the introduction of steam during the distillation is much better.

The fifth, sixth, seventh and eighth claims are to improvement in the process of purifying the crude acetone by means of lime, dilution and rectification, and these are but the steps common to all such operations.

It is upon this patent that infringement is charged, when it is simply putting into use the very old process of making acetone by the destructive distillation of acetic acid in a rotary still, as described in a paper on "Improvement in the Manufacture of Acetone," read before this New York Section of The American Chemical Society, on January 11, 1895, and published in *The Journal of the American Chemical Society* for March, 1895, p. 187, and in *An Ephemeris of*

*Materia Medica, Pharmacy, Therapeutics and Collateral Information*, Vol. IV, No. 3, p. 1653.

The writer makes acetone by the destructive distillation of the watery vapor of acetic acid in a rotary still, in the presence of barium carbonate, or pumice-stone, or bone-charcoal, barium carbonate being preferred because, being a very heavy powder, a larger charge of smaller volume can be used.

The patentees claim only acetates as their material, but claim infringement by the use of acetic acid, because acetic acid is made from acetates, and acetates are made from acetic acid; and, secondly, claim infringement on the ground that acetate of barium is first formed, and then decomposed in the rotary still, and, therefore, the process is really not a destructive distillation of acetic acid, but of barium acetate—one of the class of acetates claimed as secured to them by their patent, although in use for this purpose for so many years. That is, it is claimed that an acetate of barium is formed under conditions of temperature in which an acetate of barium cannot exist. Barium acetate decomposes at about  $400^{\circ}$  to  $405^{\circ}$  C. by an ordinary pyrometer. Acetic acid is best decomposed at about  $500^{\circ}$  to  $525^{\circ}$  C. by the same pyrometer, and yet it is claimed that, at  $500^{\circ}$  C., barium acetate forms momentarily and then is instantly decomposed. That is, it is formed in an atmosphere in which it cannot exist for an instant, and in which acetic acid cannot exist.<sup>9</sup>

<sup>9</sup> Upon this point the patentees were very decided in the statement, based not only on their own experience, but also on the experience of their German correspondents, that, if the barium carbonate was replaced by pumice-stone, the amount of acetone obtained would be too small to have any commercial importance. This result had been confirmed to them by so many trials that, at their suggestion, and in order to satisfy them that their results were not trustworthy, the following experiments were made after the above paper was written, but before it was published.

The large rotary still was emptied and cleaned out by sweeping, scraping and finally by sponging with water until it was quite free from any appreciable quantity of barium salt. It was then closed and run empty with a continuous feed of acetic acid for periods of three hours each, at the following temperatures, the rate of feeding and the assaying for acid and acetone being approximate only, and only trustworthy by averaging:

At  $300^{\circ}$  C. 22.3 pounds of absolute acid was run in, and

19.5 " " " " " received without any acetone or

any evidence of decomposition of the acid, the 2.8 pounds of acid not accounted for being the normal charge of the apparatus.

But, quite apart from this, the chemical reaction by which acetone is produced, whether from acetates or from acetic acid, was well known for more than half a century before the date of this patent. What is really covered by the patent is certain specified and de-

At 350° C. 38.3 pounds of absolute acid was run in, and  
 38.1 " " " " came through with no signs of any

decomposition—no acetone.

At 400° C. 36.1 pounds of absolute acid was run in, and  
 29.9 " " " " " received undecomposed, leaving

6.2 " " " " decomposed, and this decomposed

acid gave 97 per cent. of the acetone required by theory.

At 450° C. 35.1 pounds of absolute acid was run in, and  
 18.5 " " " " " received undecomposed, leaving

16.6 " " " " decomposed, which apparently gave

112 per cent. of the acetone required by theory.

At 500° C. 41.4 pounds of absolute acid was fed in, and  
 10.8 " " " " " received undecomposed, leaving

30.6 " " " " decomposed, which apparently gave

104 per cent. of the acetone required by theory.

At 550° C. 40.4 pounds of absolute acid was fed in, and  
 5.1 " " " " " received undecomposed, leaving

35.3 " " " " decomposed, which apparently gave

82 per cent. of the acetone required by theory.

Then a run of twenty-four hours was made at the last temperature, 550° C., to give opportunity for closer determinations of results.

32.1 pounds of absolute acid was fed in, and  
 57.3 " " " " " received undecomposed, leaving

263.7 " " " " decomposed, which apparently

gave 97 per cent. of the acetone required by theory.

The still was then opened, charged with 130 pounds of coarsely ground pumice-stone, and a parallel series of experiments made.

At 300° C. 41.8 pounds of absolute acid was fed in, and  
 39.1 " " " " " received undecomposed, leaving

2.7 " " " " decomposed, which apparently gave

33.5 per cent. of the acetone required by theory.



scribed apparatus and management, whereby an improved yield is to be obtained from acetates, and from acetates only, for the apparatus and management are not at all applicable to the use of acetic acid, and are not used either in form or substance.

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At 350° C. 39.6 pounds of absolute acid was fed in, and  
 34.8 " " " " " received undecomposed, leaving  
 4.8 " " " " " decomposed, which apparently gave

87.5 per cent. of the acetone required by theory.

At 400° C. 41.8 pounds of absolute acid was fed in, and  
 28.5 " " " " " received undecomposed, leaving  
 13.3 " " " " " decomposed, which apparently gave

97 per cent. of the acetone required by theory.

At 450° C. 41.8 pounds of absolute acid was fed in, and  
 13.0 " " " " " received undecomposed, leaving  
 28.8 " " " " " decomposed, which apparently gave

95 per cent. of the acetone required by theory.

At 500° C. 43.4 pounds of absolute acid was fed in, and  
 8.8 " " " " " received undecomposed, leaving  
 34.6 " " " " " decomposed, which apparently gave

96.4 per cent. of the acetone required by theory.

At 550° C. 43.4 pounds of absolute acid was fed in, and  
 7.4 " " " " " received undecomposed, leaving  
 36.0 " " " " " decomposed, which apparently gave

100 per cent. of the acetone required by theory.

Then a run of twenty-four hours was made at the last temperature, 550° C., as a check upon the previous results.

345.5 pounds of absolute acid was fed in, and  
 69.5 " " " " " received undecomposed, leaving  
 276.0 " " " " " decomposed, which apparently gave 104 per

cent. of the acetone required by theory.

This last and three other impossible results are, as yet, unexplainable, but they may be reasonably charged to the uncertainties in the use of an hydrometer and the iodoform process of assaying.



## ACETONE-CHLOROFORM.

The history of acetone-chloroform dates distinctly back to 1832. In the *Annalen der Pharmacie*, 1832, Vol. XXI, p. 198, Liebig describes the preparation of chloroform in large quantity, from given proportions of hypochlorite of lime, water and alcohol, and he says the yield will be equal in weight to the alcohol used. He then goes on to say that chloroform may also be obtained in large quantity by treating acetone with hypochlorite of lime under the same conditions.

Liebig does not give the yield from acetone; but after giving the yield from alcohol as being equal in weight to the alcohol used, he says it is obtained in large quantity from acetone.

In 1835, Dumas and Péligot<sup>10</sup> state that when a solution of hypochlorite of lime is distilled with wood spirit there is obtained, as a matter of fact, some ordinary chloroform. The experiment is as easy as with alcohol or acetone.

Liebig, in his text-book,<sup>11</sup> gives a formula and directions for the manufacture of chloroform from either acetone, alcohol or wood spirit, and gives to acetone the leading place.

M. Bonnet,<sup>12</sup> at a meeting of the Academy, says: "I have obtained, in the distillation of equal parts of acetate of lime and hypochlorite of lime, in a stone retort, a very large quantity of chloroform, and far more easily than by the methods of preparation that are known."

Dr. Reich<sup>13</sup> proposed and used hypochlorite of sodium in place of hypochlorite of lime, on account of the uneven amount of chlorine in the latter. He distilled together 2 pounds each of hypochlorite and acetate of sodium and received 5 to 6 drams of chloroform and 12 to 14 ounces of acetone and water. This latter was again distilled with 4 to 6 ounces of hypochlorite, and again a considerable amount of chloroform and acetone was received. The last operation was repeated with a new portion of hypochlorite, and then the total amount of chloroform was 8 to 10 ounces, with still some excess of acetone for future operations.

Acetone, when distilled with hypochlorite of sodium, yields chloro-

<sup>10</sup> *Annales de Chimie et de Physique*, Vol. LVIII, p. 15.

<sup>11</sup> *Traité de Chimie Organiques*, Vol. I, p. 576.

<sup>12</sup> *L'Institut*, No. 196, Februar 1837.

<sup>13</sup> *Archiv. der Pharmacie, Zweite Reihe*, 1848, Vol. LV, p. 65.

form in the proportion of 4 ounces of acetone to 5 to  $5\frac{1}{2}$  ounces of chloroform.

Prof. Böttger<sup>14</sup> distilled together equal quantities of commercial bleaching powder and crystallized acetate of sodium and obtained chloroform and acetone. Then he distilled the excess of acetone with a fresh portion of bleaching powder, and had "great joy in seeing from this second operation a very considerable quantity of the purest chloroform distil over, together with some acetone still undecomposed." The excess of acetone was again distilled with fresh bleaching powder and the process repeated until, by three to four distillations, all the acetone was used; the yield of chloroform being about 4 ounces to each pound of bleaching powder.

Chloroform made directly from acetone, which he says is at present (1848) to be had in the market, is obtained in the proportion of 1 ounce and 2 drams of chloroform from 1 ounce of acetone.

Still in the year 1848 (see *Archiv. der Pharmacie*, 1848, Vol. LIV, p. 23), Prof. Heinrich Wackenroder, one of the editors of the *Archiv.*, says, in substance: "The great practical interest in chloroform at the present time calls, first of all, for a closer examination of the methods for making it. Therefore, I have induced Mr. Siemerling to undertake, in my laboratory, some experiments relating to the preparation of chloroform, which are in the most recent publications on the subject. Although these experiments have, in no respect, given the results which were hoped for, it nevertheless seems to be worth while to call attention to them for the sake of the future continuation of the subject."

Then follows the paper of Mr. V. Siemerling, and at page 26: "II. Preparation of Chloroform from Acetone."

"According to the statement of Professor Böttger, 1 ounce of acetone, which has been mixed with hypochlorite of lime to a pasty mass, should give 1 ounce and 2 drams of chloroform. As this seemed to be an easy and advantageous method of preparation, some experiments were made with acetone procured from the factory of Trommsdorff, in Erfurt, but they did not accord with the statement of Böttger.

"In the first experiment (a) 30 grammes of acetone was mixed with 50 grammes of hypochlorite of lime and 50 grammes of water,

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<sup>14</sup> Polytechnisches Notizblatt, 1848, Vol. III, p. 1.

and distilled. The chloroform was separated and rectified with concentrated sulphuric acid. The yellow chloroform thus obtained was again rectified from burnt lime, when it had an empyreumatic odor—quantity not given."

In experiment (*b*) 30 grammes of acetone, 120 of hypochlorite and enough water to make a pasty mass, were mixed and distilled. It is true much chloroform came over, but there was also undecomposed acetone as well. It was repeatedly washed with water and rectified over chloride of calcium, in which rectification there was a pretty large loss every time, but the number of times is not given. The yield was 9 grammes.

Experiment (*c*), since in both experiments undecomposed acetone distilled over the quantity (proportion) of hypochlorite was increased, and 30 grammes of acetone to 150 grammes of hypochlorite, with water were mixed to a pasty mass, allowed to stand twenty-four hours, and were then distilled. The product contained much chloroform, but also undecomposed acetone; therefore, it was put back into the retort with 40 grammes of fresh hypochlorite and again distilled. The chloroform thus obtained still contained acetone, from which it was purified by repeated washing with water, and then rectified over chloride of calcium. The yield was 10 grammes of chloroform.

Another experiment (*d*) is given, wherein 20 grammes of acetone and 60 grammes of hypochlorite were distilled together without water, but with unfavorable result, the yield being 6 grammes of chloroform.

The specific gravity of the chloroform obtained from acetone, after repeated rectifications over chloride of calcium, was only 1.31, and it always contained some acetone; and the largest yield by Böttger's process was one-third of the acetone used. This differs considerably from his statement that 1 part of acetone yielded  $1\frac{1}{4}$  parts of chloroform.

Siemerling then goes on to say that if we assume, with Liebig, that acetone is composed of 1 atom of acetyloxyde and 1 atom of methyloxyde, and explain in this way the formation of chloroform from methyloxyde, it naturally follows that we must get less chloroform than the acetone used.

The sum of the elements of 1 atom of acetyloxyde =  $C_4H_6O$ , and 1 atom of methyloxyde =  $C_2H_6O$  is equivalent to 2 atoms of acetone

=  $C_6H_{12}O_2$ . In 30 grammes of acetone there are, therefore, 11.8 grammes of methyloxiide, which, since 4 atoms of methyloxiide consist of the same elements as 2 atoms of alcohol, can form 15.1 grammes of chloroform, assuming that complete decomposition takes place.

According to the theory, half of the acetone used must be recovered as chloroform; but since in the practical manufacture of chemical products the quantity prescribed by theory is never obtained, it should be considered a favorable result when one-third of the acetone used is obtained as chloroform, especially as the experiments were made only on the small scale.

From these experiments, it follows that the preparation of chloroform from acetone is quite unfit for practical use. Were even the quantity of chloroform stated by Böttger as obtainable from acetone possible, it would have the disadvantage of being freed from acetone with very great difficulty.

The paper of Siemerling, from which the above abstract is made, seems to have received the endorsement of Wackenroder, although it controverts the statements of both Reich and Böttger, and it may be from his high authority as much as from the paper itself that the results seem to have been accepted and quoted by Gmelin,<sup>15</sup> Watts,<sup>16</sup> and other reference authorities, and the influence of the publication seems to have been, so far as the literature of the subject goes, to prevent or obstruct the acetone process for many years. As it was so long and so well known, manufacturers may have been, and probably were, using the process privately; but up to 1881-1883<sup>17</sup> very little information on the subject is found. Still, the work and the conclusions of Siemerling must have been known to be grossly erroneous by every one whose interest it became to try them. Calculations would show to any one that when ordinary acetone and bleaching powder were used, the proportions required are about 1 to 10, or about double the largest proportion of hypochlorite used by Siemerling, and the resulting chloroform should be about double the weight of the acetone used; and many who preceded Siemerling knew better than he how to save and utilize the great excess of acetone or deficiency of hypochlorite taken.

<sup>15</sup> Handbook of Chemistry, Vol. VII, p. 346.

<sup>16</sup> Dictionary of Chemistry, 1883, Vol. I, p. 918.

<sup>17</sup> Sadtler, AM. JOUR. PHAR., July, 1889, p. 321.

But the Siemerling results were very faulty and very misleading in other respects. The present writer, having learned from all the work of the past on the subject that any excess of acetone used could be easily recovered and used again, added to this knowledge, from his own experience, the fact that, where an excess of acetone was taken, the hypochlorite was more economically and more promptly utilized, and the resulting chloroform was cleaner. Having gained from the Siemerling process this step, the writer was prepared to try that proportion and process critically, and he found that, as a table experiment, it was quite impracticable, by any reasonable degree of mismanagement, to obtain so low a result. In two fairly careless trials from 30 grammes of 96 per cent. acetone, the yield of chloroform was 23 grammes in one case and 32 grammes in the other, instead of Siemerling's 10 grammes. In larger trials of his proportions up to 280 pounds of absolute acetone to one cask of 1,400 pounds of 33 per cent. bleaching powder in one charge, the yield was not less than 200 pounds of chloroform, and about 130 pounds of recovered acetone, thus proving conclusively the gravity of the unaccountable errors of the Siemerling work, and showing a basis for the mischief done by this bad work.

Looking back from this later day at the authoritative way in which these mistakes and misstatements of Siemerling were published and quoted, it is easy to see that nothing could be better adapted to obstruct or prevent any increase in the general production of acetone-chloroform, and to confine its production to those manufacturers who were using the process secretly.

One of the definite evil consequences of this Siemerling paper was the adoption of its erroneous results as the basis of the following patent:

On June 23, 1886, Gustav Rumpf applied for a patent, and on July 5, 1888, patent No. 383,992 was issued to him for the invention of "a new and useful Improvement in the Manufacture of Chloroform from Acetone," of which the following is a specification: "The essential feature of this invention is based on the discovery that acetone, when treated in the proper way with a hypochlorite—for example, chloride of lime—will yield a larger quantity of chloroform than has been heretofore known. Watts, in his Dictionary of Chemistry, edition of 1883, Vol. I, page 918, says that the manufacture of chloroform from acetone cannot usefully be carried out,



not only because the price of acetone is too high, but particularly because acetone yields about 33 per cent. of its own weight of chloroform when it is treated with chloride of lime. Watts distilled 30 grammes of acetone with 150 grammes of chloride of lime, and rectified the watery distillate with 40 grammes of chloride of lime. I have discovered a method whereby it is possible to obtain a yield of chloroform from acetone very much greater than that obtained by Watts. I have found that the reaction may be made to take place in such a way that one equivalent of acetone will yield one equivalent of chloroform by volume, or about 180 per cent. by weight, and the advantages of my invention may be secured in a greater or less degree by properly employing with about 58 pounds of acetone more than 300 pounds of good chloride of lime. The best results and greatest yield of chloroform can, as I have found, be obtained by the use of, say, 58 pounds of acetone to at least 600 pounds of a good chloride of lime containing about 35 per cent. of available chlorine, and in proportion if the chloride of lime is poorer. The yield of chloroform will then be from 150 per cent. to 180 per cent. of the weight of the acetone employed, instead of about 33 per cent."

Then follow claims for invention of diluting the acetone and of introducing it periodically during the process—of introducing it below the surface of the solution in the still—of the use of a mechanical stirrer, and of the use of a still and condenser, which are described and figured.

The basis upon which this patent rests, for its reason to be, is the quotation from Watts' Dictionary. Watts quotes the process from *Gmelin's Handbook*, and Gmelin quotes it from *Siemerling's Paper* in the *Archiv. der Pharmacie*, 1848, Vol. LIV, p. 26. Now, as the paper and quotations are grossly erroneous, and as writers of preceding papers publish results that approximate those of the patent, it might reasonably be asked: what is the value of the patent? But the present writer, while intending to make acetone-chloroform, very earnestly desires to avoid all question in regard to the validity of this patent, and, therefore, uses the Watts (Siemerling) process, which is outside the limit claimed by the patent, with an entirely different apparatus and management, described by him in 1857, and republished in *Ephemeris*, Vol. IV, No. 1, p. 71.

It is proposed to use charges of 280 pounds of absolute acetone



to 1,400 pounds of 35 per cent. bleaching powder, 1 to 5—to pass the resulting chloroform through scrubbers, then distil it through water—then distil it from a small portion of bleaching powder—then pass it through sulphuric acid scrubbers, and finally rectify it in three fractions, the large middle fraction being accepted, and the others being worked over.

A part of the great excess of acetone taken in the 1 to 5 proportion is recovered by continuing the distillation after the chloroform is all over. Another part is recovered in the wash water from the scrubbers and the distillation, and the small remainder is decomposed by the small proportion of bleaching powder, the total amount recovered being practically not far from the total excess.

To this recovered acetone, carefully assayed, new acetone is added to make up the 280 pounds for the next charge.

The patentees were invited to see this apparatus and process in order to convince them that there is a strong desire to avoid any color of infringement, by taking the Siemerling proportions which are excluded from their patent. But they took the ground that this was a mere evasion, or getting round their patent by using the excess of acetone over again, and could not be made to see that this, if objectionable, is so by defect in the equity of the patent, and is a proceeding that antedated the patent by many years. And finally, they covered everything by claiming that the patent secured to them the sole right to make chloroform from acetone in the United States, thus claiming a reaction that had been well known for more than fifty years.

As to the reasons why large manufacturers of chloroform did not avail themselves earlier of the acetone process, the first answer is that it is probable that many of them, in Germany, at least, did so secretly as soon as acetone became cheaper than alcohol.

But as to other more positive reasons, the writer, as having been for many years a large manufacturer from alcohol, and as having, with all other makers, given up the manufacture rather than contest this patent, can only speak for himself. He for many years doubted the identity of alcohol and acetone-chloroform, and doubted whether the latter was as easily purified for use as the former, so that when chloroform was offered to him at so low a price as to insure that it was made from acetone it was refused. Chloroform has always been a most important agent, and during the early part of

its career the numerous fatalities from its use were charged to its impurities, so that the alcohol process was adhered to until the identity of the products from alcohol and acetone was fully proved—not only chemically, but also by surgical experience of considerable duration. Then as time passed and the subject came up for research and reconsideration, the Siemerling results came up also and settled the question against acetone.

Finally, Dr. Gustav Rumpf, a German, and an employee for some years in an acetone-chloroform manufactory in Germany, where there is no patent, came to this country, took out these patents and assigned them to the present holders, so that now, for the past seven years or more, any one making acetone-chloroform in this country, by processes that had been free and largely used in Germany for many years, was liable to prosecution for infringement.

Having any general knowledge of the history of acetone and acetone-chloroform, it is difficult to understand how such patents could be issued that would claim to control the proportions of well-known chemical materials in long-known chemical reactions. But such patents were issued, and, therefore, command respect. That the processes were not used earlier in this country may be charged chiefly to the endorsements of the Siemerling paper; and that the patents appear to have been so long acquiesced in is due to the circumstance that any one who might contest them would do so at great cost of money, time and annoyance in defensive litigation which, if successful, would secure the benefits equally to many manufacturers and to the public in lower prices of the products, whilst the contestant would bear all the costs.

In seeking new outlets for acetic acid, the writer determined to convert the acid into chloroform, and determined also to respect these patents. In the intermediate step of making acetone, acetic acid was used, not to evade the patents, but because by its use the impurities of the crude acetates of lime were avoided, and a larger yield of better acetone was obtained. In the use of acetic acid instead of the acetates of the patent an entirely different apparatus and management are required and used, and if the patent did not exist the writer would not use either its apparatus or management, but would prefer the rotary still and the continuous process.

With regard to the other step, wherein the acetone is converted into chloroform, this is accomplished by a reaction that was long

and well known before the date of the patent, and the proper proportions of the materials required for the reaction were easily obtainable by calculation, and this knowledge also antedated the patent. The patent then simply covers a specially devised and described apparatus and management which the writer does not use, and does not want to use, even if they were not patented, but much prefers his old form of apparatus and management described in 1857, and used for many years in making alcohol-chloroform; and the successful use of this apparatus and management for acetone-chloroform is simply in accordance with the statement of Liebig, in 1832, that acetone could be successfully used under the same conditions as alcohol.

### SOME CONSTITUENTS OF THE ROOT OF *POLYGONUM CUSPIDATUM*.<sup>1</sup>

By A. G. PERKIN, F.R.S.E.

Among the different varieties of the species of *Polygonum*, that best known is perhaps the *P. tinctorium*, the leaves of which are used as a source of indigo in China, Japan, and some parts of Russia. Of others, the *P. aviculare* and *barbatum* yield a blue color, probably indigo, and the *P. hydropiper* and *tortosum* are said to contain a yellow coloring matter; moreover, the roots of some of these varieties possess medicinal value.

The *P. cuspidatum*, which is common in parts of India, China and Japan, has evidently attracted but little attention, the only reference found bearing on its properties being the following, contained in a paper (*Journal Royal China Branch of Royal Asiatic Society*, 22, New Series, No. 5, 1887), by A. Henry, M.A., L.R.C.P., entitled "Chinese Names of Plants," "*Kan-yen, wu-tzu*, name at Patung for the root of *P. cuspidatum*, which is said to be used for dyeing yellow."

The roots, which somewhat resemble those of madder and morinda, vary in diameter from  $\frac{1}{4}$  inch to 1 inch when fresh, and consist of a thick, succulent bark, internally of an orange-red color, and a central light yellow woody portion; the former, on drying, shrivels considerably and becomes lighter in tint.

<sup>1</sup> Abstracted by J. C. Peacock from the *Journal of the Chemical Society*, December, 1895.

As examination showed that the woody portion contained but little extractive matter, the bark only was employed.

The ground root bark was extracted with boiling alcohol, and the resulting orange-brown extracts evaporated to a small bulk. This was treated with water and extracted with ether, which removed small quantities of emodin and wax. An addition of baryta water to the aqueous liquid produced a dirty white precipitate, which was removed by filtration. The deep red filtrate, after being neutralized with acetic acid and saturated with common salt, was extracted with a large volume of ethylic acetate, and the extract evaporated. This treatment furnished a product which appeared under the microscope as a mixture of gelatinous and crystalline matter. This mixture was dissolved in boiling alcohol. On evaporating to a small bulk and cooling, the liquid deposited a gelatinous matter; directly this ceased to form, it was rapidly filtered, and the crystalline substance which separated from the filtrate was collected and purified by crystallization from acetic acid. It then consisted of a glistening mass of orange-yellow needles, which, when heated, softened at  $200^{\circ}$  and melted at  $202^{\circ}$ – $203^{\circ}$ . It is but sparingly soluble in ethylic acetate, boiling water and boiling alcohol. From its solution in the last solvent it is deposited in a gelatinous condition if rapidly cooled, but when left to cool slowly it separates as a bulky mass of hair-like needles. It is almost insoluble in ether. With cold dilute alkalis or baryta water, it yields orange-red liquids, and by treating a boiling alcoholic solution of the substance with alcoholic potash, the potassium derivative separates, on cooling, in the form of red, flat, microscopic needles. The lead salt, an orange-red amorphous powder, somewhat soluble in boiling water, is formed, when lead acetate is added to an alcoholic solution of the substance.

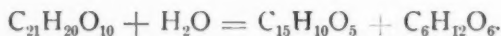
Analyses of the crystals gave the following numbers:

				Required for $C_{21}H_{20}O_{10}$
Carbon . . . . .	58.28	58.48	58.48	58.33
Hydrogen . . . . .	4.92	5.04	5.02	4.63

Experiments showed the substance to be a glucoside, and, in order to determine its nature, a solution in 60 per cent. alcohol was digested at the boiling heat with a small quantity of hydrochloric acid. During this operation, the light yellow liquid became orange-red, and crystals separated. Water was added, the mixture allowed

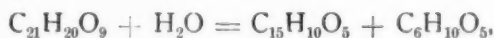
to cool, the product collected, washed with water, and dried at 120°. It formed orange-red needles, readily soluble in alcohol. They melted at 253-254°, and sublimed at higher temperatures with partial carbonization. A study of the decomposition products and derivatives of the substance showed it to be emodin, which exists in rhubarb root and also in the bark of *Rhamnus frangula*, as a glucoside (Trans., 1892, 61, 1, Thorpe and Miller).

A determination of the amount of emodin produced by the hydrolysis of the glucoside gave 61.82 per cent. as the result. This is in accordance with the following equation, which requires 62.50 per cent.



The filtrate from the emodin, after neutralization with silver carbonate, and evaporation, yielded an almost colorless syrup, which reacted with phenylhydrazine acetate on gently warming, lemon-yellow aggregates of an osazone being deposited on cooling.

Frangulin, the only glucoside of emodin hitherto known, and found in *Rhamnus frangula*, is not identical with the above. When hydrolyzed, for instance, it yields emodin and rhamnose (Thorpe and Miller, *loc. cit.*),



a reaction which requires 64.9 per cent. of emodin; and its difference in composition ( $\text{C}_{21}\text{H}_{20}\text{O}_9$  requires C, 60.57; H, 4.80), crystalline appearance, solubility and other properties from the glucoside found in *Polygonum cuspidatum*, show clearly that they are distinct substances. Polygonin is the name proposed for this new glucoside of emodin.

The gelatinous residue obtained during the purification of the polygonin had the properties of a glucoside, and, upon hydrolysis by digestion with dilute hydrochloric acid, yielded emodin, and a second substance which differed from emodin by melting at 199°, and by being sparingly soluble in alcohol and insoluble in dilute ammonium hydrate. This substance was identified as emodin monomethyl ether, which has been found to exist in the root bark of *Ventilago madras-potana* in the free state (Perkin and Hummel, Trans., 1894, 65, 932).

It is interesting to note that Schwabe (*Arch. Pharm.*, 1888, 26, 569), and subsequently Thorpe and Miller (Trans., 1892, 61, 6), isolated from the bark of *Rhamnus frangula*, not only frangulin, but a



second substance, to which they respectively assigned the melting points  $199^{\circ}$  and  $202^{\circ}$ – $203^{\circ}$ , and this was considered by the latter authors to be probably a trihydroxymethylanthraquinone isomeric with emodin. The properties of this substance agree very closely with those observed in this investigation for emodin monomethyl ether, and it appears possible that they may be identical.

The ethereal extract obtained during the isolation of the polygonin was extracted with dilute alkali, which removed an exceedingly small quantity of emodin. The remaining ethereal solution, upon evaporation, left a wax which, after recrystallization from boiling alcohol, was obtained in beautiful, colorless leaflets, which resembled phenanthrene in appearance, and melted at  $134^{\circ}$ – $135^{\circ}$ . A combustion gave:

		Required for $C_{18}H_{28}O$ .
Carbon . . . . .	83.19	83.08
Hydrogen . . . . .	11.60	10.75

This result and its physical properties make the wax identical with that of the root bark of *Morinda umbellata* (Perkin and Hummel, Trans., 1894, 65, 867).

Dyeing experiments with the roots, using mordanted calico, showed, as was to be expected from the chemical examination, that it was devoid of useful tinctorial properties; faint, dull shades were obtained, evidently due to the presence of a small quantity of tannin matter. It is thus evident that no yellow coloring matter is present in this portion of the plant. Examination, however, showed that the leaves contain a small quantity of a substance which yields yellow shades with alumina mordant, and it is possible that some confusion has arisen between the leaves and the root with regard to this property.

A new serum has been brought out by the New York Biological and Vaccinal Institute, known as *Gibier's Double Antitoxin*, which contains the diphtheria and streptococcus antitoxins, obtained from one horse immunized against both infections.

An investigation of *Bismuth Subnitrate* has been made and reported by Dr. Charles O. Curtmann, of Pharmacopœia Research Committee D. The conclusions arrived at are that nearly all commercial specimens are more basic than is demanded by the usually accepted symbolic formulæ, or else they are mixtures, in indefinite proportions, of bismuth hydroxide with the true subnitrate. The latter is most likely the correct view.



## EDITORIAL.

## ROENTGEN'S RAYS.

Considerable attention has recently been excited in scientific circles by what is popularly designated as *Roentgen's Discovery*.

Professor Wilhelm Conrad Roentgen, of Wurzburg, Germany, noticed that the light of an induced electric current in a Crookes' tube affected a photographic plate that was enclosed between two wooden slides. In other words, he found a light capable of penetrating wood. He immediately instituted a series of investigations by which he demonstrated that it is possible to photograph through many substances that are opaque to ordinary light; wood, flesh, leather, paper and certain metals are the most conspicuous substances which he found to be transparent to these rays.

These phenomena have since been investigated by a number of other physicists, and Roentgen's observations have been confirmed.

Mr. Campbell Swinton, in London, demonstrated that, among the metals, aluminum is especially transparent to these new rays. He placed two aluminum trays between the source of these rays and a photographic plate; one of the trays contained a solution of alum and the other a solution of iodine in carbon disulphide. It is known that alum solution absorbs ultra-red, and iodine solution ultra-violet rays of light. The conclusion reached by Mr. Swinton was that the new light contains rays which are absorbable by iodine, and it is probable that they are ultra-violet rays.

In this country, Professor Wright, of Yale University, found that with many substances strong impressions were obtained upon a photographic plate even when it was enclosed in an opaque wrapping of black paper and covered with a piece of pine board one-half inch in thickness.

One of the most peculiar observations made on this light is that glass is more opaque than many of the metals, while ebonite, which is practically opaque to ordinary light, is transparent to the new rays.

The term X-rays has been provisionally applied to this new form of energy.

On another page we give the results of some experiments by Professor E. S. Bastin, of the Philadelphia College of Pharmacy, on the presence of these, or similar, rays in sunlight. His experiments were made on the 17th of February, and we believe he is among the first to announce positive results from sunlight, although so rapidly is the study of Roentgen's discovery progressing, he may be anticipated by some one else before his paper can appear in print.

It is too soon to predict the uses to which these X-rays may be applied, but it is already evident that the bones in the living subject may be examined by them, since flesh is transparent to them, while bone is opaque. No doubt the discovery will be of some use in surgery; in fact, it is claimed that a number of successful operations have already been performed in which foreign bodies have been first located by the aid of these rays. In Berlin the photograph of a man's hand revealed the presence of a piece of glass that had been imbedded in the flesh for years. Defects in metal castings may be detected by this light; hence, it is thought it will be especially of service to indicate flaws in large guns.

Professor Bastin hopes to study the structure of living plants by these rays, if he is so fortunate as to find that some tissues are opaque while others are transparent.

THE METRIC SYSTEM IN THE UNITED STATES.

We have received a communication from the American Metrological Society, whose headquarters are at Columbia College, New York, concerning a bill which is now before Congress for the compulsory introduction of the metric system in the United States.

The bill has passed second reading in the House, and has been referred to the Committee on Coinage, Weights and Measures. The following is a copy of the bill :

"A Bill to fix the standard of weights and measures by the adoption of the metric system of weights and measures.

"Be it enacted by the Senate and House of Representatives of the United States of America in Congress assembled, That from and after the first day of July, 1897, all the departments of the Government of the United States, in transaction of all business requiring the use of weight and measurement, shall employ and use only the weights and measures of the metric system, as legalized by Act of Congress approved July 28, 1866.

"SEC. 2. That from and after the first day of July, 1899, the metric system of weights and measures shall be the only legal system of weights and measures recognized in the United States.

"SEC. 3. That the tables in the schedules annexed to the bill authorizing the use of the metric system of weights and measures, passed July 28, 1866, shall be the tables of equivalents which may be lawfully used for computing, determining and expressing in customary weights and measures the weights and measures of the metric system."

The United States could not take a wiser step on this subject than make this bill a law. Unless some such decisive action is taken, the country will drag through another century with a system of weights and measures which is as inconvenient as it is unpractical.

The only way to adopt a system like this is to place the weights and measures in the hands of those who are to use them; the whole thing then becomes ridiculously simple.

Those who are in sympathy with this movement should write to the Hon. C. W. Stone, Chairman of the Committee on Coinage, Weights and Measures, and signify their approval of House Bill No. 2,758, introduced by the Hon. Mr. Hurley.

THE LIBRARY OF THE PHILADELPHIA COLLEGE OF PHARMACY.

Mr. Howard B. French has recently presented to the Library of the College some 2,500 volumes from the library of the late Dr. Ruschenberger. This magnificent donation brings the total number of volumes in the Library up to about 10,000.

REVIEWS AND BIBLIOGRAPHICAL NOTICES.

ETIDORHPA, OR THE END OF EARTH. By John Uri Lloyd. Second edition. The Robert Clarke Company, Cincinnati, 1896.

About four months ago, Professor Lloyd issued the author's edition of this book to those who had been so fortunate as to previously subscribe for it. He soon found, however, that there were a large number of disappointed people who had been unable to secure copies of the work, and that the only recourse left for him was to issue a second edition. This he has done, and the result is

a volume which is a credit to both author and publishers. Two new illustrations have been added to this edition, otherwise its pages bear a close resemblance to those of its predecessor. Neither edition was issued for personal gain, and the author pledges himself to place any profit to the credit of the Lloyd Library, which will eventually be devoted to public educational purposes. We predict that the author will find the second edition exhausted almost as readily as the first.

**SELECT EXTRA-TROPICAL PLANTS.** By Baron Ferd. von Mueller. Ninth edition. Robert S. Brain, Government Printer, Melbourne, Australia, 1895.

The object of this work is to bring together some condensed data in popular language on all the principal economic plants hitherto known to prosper beyond the equinoctial zone. Information of this kind is widely scattered, and often only accessible through voluminous and costly works in various languages.

In 654 octavo pages, the author has condensed an immense amount of useful information. His lucid literary style has made the book very readable, and his judicious selection of all extra-tropical plants which have any present or prospective value, makes it almost an encyclopædia of economic botany. No geographical section is especially favored, one can find the useful plants at his door in this country as fully described as those growing in Australia or India.

**PRACTICAL STUDIES IN FERMENTATION**, being contributions to the life history of micro-organisms. By Emil Chr. Hansen, Professor and Director of the Carlsberg Physiological Laboratory, Copenhagen, translated by Alex. K. Miller. London: E. & F. N. Spon; New York: Spon & Chamberlain, 1896.

The investigations brought together in this book treat in the main of the great questions of the circulation in nature of the alcoholic fungi, their relationship to the diseases of beer, the pure cultivation of yeast and the employment of systematically selected species and races. In the first chapter the author gives some historical data concerning the introduction of pure yeast cultures into the brewing industry, which he accomplished over twelve years ago. The results at first were of doubtful utility; but gradually, as more information was gained, it was found that objectionable bacteria were not alone the cause of some of the commonest and most serious diseases of beer, but that turbidity and objectionable changes in flavor were frequently caused by certain species of yeast. It was found, therefore, "that the pitching yeast should consist only of a single species, namely, that best suited to the brewery in question."

The author then gives a brief account of his own method of pure cultivation, and points out how his theories and practice differ from other well-known investigators, notably Pasteur. Altogether, it is a book full of interest, not only to those connected with the brewing industry, but to everyone interested in fermentation and the natural history of micro-organisms.

**FORMULAIRE DES MÉDICAMENTS NOUVEAUX POUR 1896.** Par H. Bocquillon-Limousin. Avec une introduction par Henri Huchard. 7<sup>e</sup> édition. Paris: J.-B. Baillière et Fils.

Everyone interested in the newer remedies will examine this book with profit. The most notable novelties for this year are: Aïrol, Apolysine, Argonine, Benzacétine, Cannabindone, Caséinate de fer, Citrophène, Cotarnine, Cristallose, Cuprohémol, Dihydrorésorcine, Eudoxine, Ferripyrine, Gallicine,

Hémogallol, Hémol, Hypnoacétine, Lysidine, Nosophène, Pain d'aleurone, Périodure de thalline, Phosphergot, Pixol, Résorbine, Salantol, Salithymol, Sublimophénol, Tannigène.

It is not only the very new remedies that have received attention, but some older ones; for example, there are four formulas given for paregoric. The volume for 1896 is fully up to its predecessors.

NOTES ON A FEW PYRIDINE ALKYL IODIDES. By Albert B. Prescott. Reprint from the *Journal of the American Chemical Society*, January, 1896.

DIPYRIDINE TRIMETHYLENE DIBROMIDE, and A STUDY OF CERTAIN ADDITIVE REACTIONS OF ORGANIC BASES. By R. F. Flintermann and A. R. Prescott. Reprint from the *Journal of the American Chemical Society*, January, 1896.

CONSTANTS OF THE ELEMENTS, AND TABLE OF CHEMICAL CLASSIFICATION. Two charts prepared by Wm. H. Seaman, M.D., Washington, D. C.

## MINUTES OF THE PHARMACEUTICAL MEETING.

PHILADELPHIA, February 18, 1896.

The regular Pharmaceutical Meeting was held in the Museum of the College at 3 o'clock. Mr. Joseph W. England was chosen chairman, and the minutes of the previous meeting were ordered to stand as published.

The presentation to the College Library of about 2,500 volumes by Mr. Howard B. French was announced by the Registrar. This valuable addition to the library comprises works on medicine, pharmacy and allied subjects, and increases the total number to about 10,000 volumes.

The chairman presented to the Museum, on behalf of Messrs. John Wyeth & Bro., a specimen of "red gum," which is a product of *Eucalyptus rostrata*. It is soluble in both alcohol and water. The tincture does not gelatinize, and its peculiar adhesive property, when applied to the mucous membrane, renders it efficacious as a local astringent. It has also been recommended for seasickness (*AM. JOUR. PHARM.*, 1890, p. 347).

The first paper, entitled "The Shaddock, or Grape Fruit, and Some of Its Applications in Pharmacy," was read by Mr. Lyman F. Kebler, on behalf of Mr. Charles H. LaWall, the author. (See page 121.) This paper is an interesting one, and it is a valuable contribution to botanical literature, as the history of this member of the *Citrus* genus is extensively reviewed, and many conflicting statements contained therein brought to notice. The botanical characteristics of the members of the group are also fully considered, in order to establish, as far as possible, the identity and relationship of the different varieties. It was accompanied by samples of the fruits, including both those having a white pulp and those having a red pulp, and known by the vernacular names of Adam's apple, grape fruit and forbidden fruit; and, also, by photographs from Sandford, Fla., illustrating the appearance of the trees during the fruit-bearing season, and a specimen of grape fruit wine from the same locality, both of which were presented by Miss Bertha L. De Graffe.

The chairman remarked upon the merits of the paper, and said he was sure that he voiced the sentiments of the meeting in expressing his regret for the absence of Mr. LaWall.

Professor Trimble spoke of the possibilities of this fruit in pharmacy, and

also of the amount of work required in preparing such a paper, in consulting various works of reference, and that Mr. LaWall had found it advisable to make two papers, and report at another time on the chemistry of the subject.

Professor Bastin gave as his opinion that some of the varieties are probably hybrids with the orange family, and that the shaddock proper bears a resemblance to the orange both in appearance and taste, and, as the plants have been cultivated from time immemorial, it is very difficult to distinguish the species.

The next paper, entitled "Bitterless Cascara Sagrada," was read by Professor Remington, upon whose request it was contributed by Mr. Henry B. Gilpin, of Baltimore. (See page 135.) Professor Remington spoke of Mr. Gilpin's liberality in thus consenting to publish a formula which has particular significance when considered from the commercial standpoint. Samples of the aromatic powder and of the aromatic bitterless fluid extract were shown, and the quality of these preparations could be judged from their fine appearance.

Mr. W. L. Cliffe commented favorably upon the process of macerating the drug with magnesia and water before drying, to neutralize the bitter principle, and said that the same object could not be attained with the use of dilute alcohol.

Professor Trimble wished to know whether any of those present had tried the use of ammonia instead of magnesia. Mr. England said that he had used it to advantage in the preparation of the syrup.

The last paper on "The Use of Oxalic Acid in Preserving the Color of Plants," was presented by Mr. J. Henry Schroeder. (See page 132.)

Mr. Schroeder exhibited an interesting collection of specimens, including plants, the colors of which are the most difficult to preserve. These were collected last summer, and were preserved by pressing with a paper which had been saturated with a 3 per cent. solution of oxalic acid and dried.

Professor Bastin said that it was difficult to get such good results ordinarily, and that it was exceedingly important and desirable to find a preservative agent for the color of plants. He recommended selecting specimens of Baptisia and Salix for carrying on experiments, as the leaves of these plants very readily blacken, and suggested that two sets of specimens be prepared, one with the use of acid paper and the other without it, in order to demonstrate the utility of the method. He also advised exposing the specimens to the influence of light to determine the stability of the colors.

Mr. Schroeder, in replying to a query from Mr. Wallace Procter, said that the blue color of flowers is not affected by the presence of oxalic acid.

Mr. Procter showed samples of lard, beef and mutton suet and goose-grease, which were presented by Mr. Snyder, of the Snyder Pharmacal Company, of New York. These fats are said to be anhydrous and quite pure. The lard is made from leaf fat only, which is brought from the West during cold weather, and is obtained from hogs of medium size and corn-fed. The membranes are removed from the fat and it is put into a Miles cutter, which reduces it to the appearance of lard. Then it is washed and rendered with steam at a temperature not exceeding 212° F.; filtered through paper in a filter-press, heated *in vacuo*, to remove water, and agitated while cooling, with access of as little air as possible.

Mr. Kebler made a statement in reference to the tests for gurgun balsam. (See page 143.)

On motion, the meeting adjourned.

THOS. S. WIEGAND, Registrar.

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OPUNTIA VULGARIS IN FRUIT.